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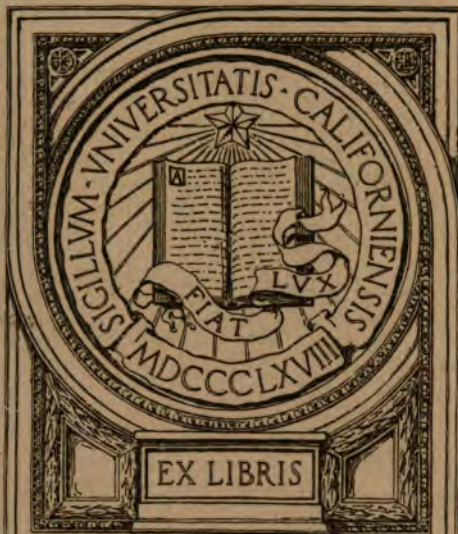
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**A STUDY OF NICKEL FERROCYANIDE
AS A MEMBRANE IN THE
MEASUREMENT
OF OSMOTIC PRESSURE**



Dissertation presented to the Board of University Studies
of the Johns Hopkins University in conformity with the
requirements for the Degree of Doctor of Philosophy.

JOSEPH LLEWELLYN MCGHEE

B. D. SMITH & BROS., PRINTERS, PULASKI, VA.

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ACKNOWLEDGMENT.

For the kind helpfulness of Pres. Remsen, Prof. Morse, Prof. Jones, Prof. Acree and Prof. Whitehead the writer wishes to express his appreciation, but because so much of inspiration, information through personal instruction and a better appreciation of the highest ideals put to practice in research work came to the author through Prof. Morse, it is to him chiefly that credit is due for whatever merit or value may be found in these pages.

He is also indebted to Prof. Renouf for courtesies shown.

For all kindness received from his co-workers in the laboratory full indebtedness is hereby acknowledged.

BIOGRAPHY.

J. L. McGhee, born in Loudon County, Tennessee, in 1873. Reared mostly in Virginia. High School work at Pearisburg Academy and at Hiwassee. A. B. degree at Emory and Henry College, Emory, Virginia, 1903. Graduate work at the University of Chicago. Head of the department of Chemistry at Emory and Henry College.

A STUDY OF NICKEL FERROCYANIDE AS A MEMBRANE IN THE MEASUREMENT OF OSMOTIC PRESSURE.

Dependence upon work previously done in this laboratory for the development of the present investigation is fully recognized. A brief statement of this pre-requisite work seems necessary in order that the connection of the whole may be properly set forth.

When the electrolytic process for the deposition of membrane was first devised, about twenty-five colloidal substances were tested to secure the one best adapted to osmotic pressure. Among those showing most promise were copper ferrocyanide, nickel ferrocyanide and several others.

These tests were largely qualitative owing to the scarcity of suitable cells, manometers, thermostats and other devices for quantitative work. Thus limited and the task being such a stupendous one, the copper ferrocyanide membrane was the only one used extensively.

Although some work had been done to determine the relative value of other colloids, it had not the advantage of recent improvements, until the present year.

THE CELL.

Although the preparation of suitable cells preceded the present work, it is in order to give more than a brief mention of the troubles encountered and of the methods used to overcome the difficulties. For obviously no membrane for measuring osmotic pressure is of any use without a proper cell in which to place it. Likewise numerous other requirements will be noted more or less briefly.

The ordinary cell of the potter does not serve in measuring osmotic pressure for the following reasons or causes:

1. They do not possess the strength necessary to withstand the outward pressure; most of them crack under pressures below 20 atmospheres.

2. They contain "air blisters," which communicate with various portions of the cell wall and permit the formation of irregular, secondary membranes, situated somewhat in parallel and at varying distances from the inner surface. Any considerable pressure brought upon a membrane deposited in such a cell is sure to break through the colloid.

3. The potter's cell also lacks uniformity in its pores, an indispensable property in suitable cells. This requirement appears with more force when it is considered that the membrane is deposited where the opposing ions meet, and that the part of the cell wall in which they meet is determined largely by the size of the pores in the cell. This will be presented more at length under the discussion of the membrane.

To secure a cell combining the necessary strength and uniform porosity required several years of persistent work. Early attempts to increase the strength of the material by adding feldspar were not satisfactory because uniform porosity was not secured at the same time. This was true even when every care was used to properly wash, bolt, mix, dry and bake.

Finally a suitable combination of clays, one deficient in binding material and another over-rich in such constituents, was tried with success; producing a cell of uniform texture in every respect, so far as known.

The upper half of the cell is glazed, inside and outside. For this purpose a glaze is required whose coefficient of expansion equals that of the cell itself. A suitable glaze was finally obtained by mixing silica and feldspar with one of the better grades of glaze used by the potter.

Before the cell is glazed it is carefully ground on the lathe to fit the brass collar and the cone shaped stopper of the manometer attachment. The general shape of the cell is that of an inverted frustrum except at the top where a shoulder is left to rest upon the collar that fastens together the cell and the manometer. The upper and lower surfaces of the shoulder are carefully turned on the lathe perpendicular to the longitudinal axis of the cell so that the pressure from the collar may be evenly distributed to prevent crushing when the cone of the manometer is screwed into place. Equal care is used in cutting all parts of the cell, which must not be too wet or too dry.

The upper part of the cell is made larger to prevent the outward pressure of the cone from splitting the cell, and also to avoid crushing by the cylindrical collars.

The lower part of the brass collar upon which the cell rests during a measurement is extended inward and covered with lead in order to afford a cushion for the cell shoulder under pressure, and a cylinder of the proper size is selected for each cell so that the cell shoulder may not be chipped off by one that is too large; or that the cell may not be crushed by one that is too small.

The upper half of the brass collar is quite heavy. This is required because a slot is left in it to admit the manometer tube, as the collar cannot be slipped over the manometer from the top. The middle portion of the upper cylinder is extended inward in a carefully turned shoulder that rests on the top of the cell. In this way pressure is applied without injury to the cell or to the manometer.

The brass cone of the manometer is covered by rubber tubing of the best quality, securely tied with several strands of waxed shoemaker's thread at the top and bottom, more thread being used at the top, where the last strands extend down to the mouth of the cell, when the cone is screwed into place.

(For a full statement of the manufacture of cells employed in osmotic pressure, the reader is referred to the American Chem. Journal of Feb., 1911.)

THE REMOVAL OF AIR FROM THE CELL WALL.

All air must be removed from the pores of the cell wall before membrane is deposited, in order to secure uniformity and strength. This removal of air is accomplished by the electric current passing from a platinum anode surrounding the lower unglazed portion of the cell, through an electrolyte of lithium sulphate to a platinum cathode placed inside the cell. The large capacity of the lithium ion for water produces an ion of such size that all air is removed in about six hours, from a cell of average density. During this process lithium hydroxide accumulates at one electrode and sulphuric acid at the other.

By mixing the two solutions repeatedly the lithium sulphate is again ready for use.

Before membrane is deposited the lithium sulphate is removed from the cell wall electrolytically, pure water being frequently added to replace the base and acid as they accumulate about the electrodes. When the salt is all removed the cell is ready to receive the membrane.

THE DEPOSITION OF THE MEMBRANE.

A bath regulated to a definite temperature is now required. This is secured by the use of both gas and electricity. Gas supplies heat to raise the water nearly but not quite to the desired temperature. Electric stoves with thermo-regulators supply the margin of difference.

In the bath a stirring apparatus is run by a small motor. The stirrer is placed in the upturned opening of an iron or brass tube lying in the bottom of the bath and extending its entire length, thus securing adequate mixing of the water and uniform temperature in every part of the bath. For higher temperatures the bath is fully covered to prevent evaporation and loss of heat.

Into glasses set in the bath water are placed cylindrical nickel anodes. A solution of tenth normal nickel sulphate nearly fills the glasses. A platinum cathode and a tenth normal solution of potassium ferrocyanide are placed inside the cell, which is provided with a funnel and exit tube held in place by a two-hole rubber stopper. Through the funnel fresh potassium ferrocyanide solution, kept at the bath temperature, is poured every third minute during the deposition process. This prevents the accumulation of alkali inside the cell which would dissolve the membrane if not removed.

The position of the membrane in the cell is a matter of great importance. With the very slow diffusion which would exist in the wall between a membrane in the mid-wall position and the solution within the cell, it would be impossible to secure a proper determination of osmotic pressure. Another objection to a mid-wall membrane is that great uncertainty would exist about the state of such membrane in that section of the cell between the outer and inner glaze, above the portion

which is supposed to be the upper limit of the membrane as now deposited. This will appear more clearly from what follows.

While a mid-wall membrane is unsatisfactory, it is equally so with one produced by surface precipitation. In the latter case the membrane is not strong enough to withstand pressure or to prevent flaking off. In order to secure the membrane to the cell wall, the porosity of the cell wall and the voltage of the electricity had to be so adjusted by experiment to the rate at which the nickel ion and the ferrocyanogen ion penetrated the cell wall, that they would meet just within the wall surface on the inner side, where practically no hindrance to the diffusion of entering-water, with the solution in the cell, is possible. Thus deposited the membrane is satisfactory in every way so far as experience has gone. A voltage of one hundred and ten to one hundred and fifteen seems best for this purpose.

During the deposition of the membrane in each cell a record of amperage is kept and the resistance of the membrane in any cell can be determined. After receiving membrane an hour or so the cell is removed, washed and soaked for a day or two in a water solution of thymol to remove all nickel sulphate and potassium ferrocyanide and small amounts of any electrolytes that might be present as impurities in the cell wall. The temperature of the cell is permitted to change as little as possible. Thymol is used as a disinfectant to prevent the growth, especially, of penicillium, which seems to feed upon the nitrogen of the colloidal compound, thus destroying the membrane. The cell is kept in this thymol solution until it is placed again between the electrodes for more membrane, or till it is ready to be set up for a measurement. Usually the first attempt to use a membrane for measuring osmotic pressure is not successful. The cause is supposed to lie in the need that the membrane be packed or compressed by use until sufficiently firm; repeated additions of the colloid being made in the meantime. Thus the weakest places are broken through and are the ones first filled or mended when membrane is again deposited, as the current passes through the ruptured places most abundantly.

Repetition of the above processes produces a suitable membrane in about two months, on the average, if the whole of the large number of necessary conditions is met.

It was found in the present work that commercial aluminium which was used as racks for holding the cells while in soak left a deposit in the thymol solution. Tests showed this to be in part some compound of aluminium, probably the hydroxide, and was doubtless the result of primary couples set up between the aluminium and small particles of other metals present as impurities. Evidence of this was found in small pits that appeared in the aluminium. These racks were discarded. The cells are now placed in large desiccators which are kept in the baths, and provided with woolen hoods over the tops to prevent radiation of heat.

Great care is taken to avoid any dilution or concentration of the cell contents. This may occur either in the failure to have the whole cell and its attachment at the proper temperature when set up, or it may be caused by the contraction or expansion of the mercury in the manometer, due to a considerable difference between the temperature of the bath in which it is placed during the measurement, and the room temperature when set up. It is impossible to have the whole manometer at the temperature of the experiment when being set up, especially while working at very high or very low temperatures.

If the cell and the solution are too cool when set up, expansion occurs as the proper temperature is reached, water passes out of the cell, leaving the solution concentrated. The resulting pressure developed is higher than the intended conditions would give.

On the other hand, if the cell and its contents are too warm when set up, contraction takes place, water is forced through the membrane as the cell is brought to the cooler temperature of the experiment, resulting in dilution of the solution and a lower pressure than the true one for the desired conditions.

Every precaution is necessary to prevent leakage of the solution from the cell while under pressure. The various means used for this are the following: The cell neck is so ground as to receive the cone shaped stopper which has a definite taper.

This cone is made of heavy brass. Through the cone are passed the capillary manometer tube and a small metallic tube which connects with the inside of the cell. After any air bubbles and the excess of solution pass out through this tube, it is closed by a metal screw plug which fits upon an oil-soaked washer. The washer is kept from spreading by making the contact surface of the plug slightly concave. For temperatures under 50° these two tubes are fastened to the cone by "Wood's metal." By use of the plug referred to and the cylindrical screw collar already described, it is possible to adjust the cell to any initial pressure desired. In this way the dilution of the solution which would occur by permitting the whole pressure to develop by osmosis is prevented. Great caution is used in this, however, in order to avoid too great an initial pressure.

After all the precautions mentioned above are taken, the time required for the actual process of setting up the cell is only a few minutes. This is essential for successful measurement of osmotic pressure. The manometer cone is forced into the cell, screwed as tightly as desired, the nut inserted into the top of the small tube that connects with the inside of the cell, and the cell is placed in hundredth normal solution of nickel sulphate. In the sugar solution within the cell is placed an osmotically equivalent amount of potassium ferrocyanide. The liquid inside and outside the cell is a thousandth normal solution of thymol in water, to which these other substances are added.

The whole apparatus is next placed inside of an enclosed constant temperature bath described later of such construction that the water below and the air above are both kept at the same temperature.

THE MANOMETER.

Before the manometer is ready for use an incredible amount of the most careful work must be done upon it. Adequate description of this part of the work can not be given here. The reader is referred to the American Chemical Journal of March, 1911, where the subject of manometers is not only presented but illustrated in a most satisfactory manner by Prof. Morse, Dr. Holland and Mr. Carpenter. The only part taken by the writer

in the manometer problem was the horizontal calibration of manometers ①, ②, ④, and ⑤ which suggested a slight improvement in manipulation.

After the manometer tube has the "scratch" (a mark for reference) etched upon it, a short column of purest mercury is put into the thoroughly clean, dry tube. The latter is fixed horizontally upon the dividing engine, and over a mirror scale of millimeter divisions. Placing one end of the short mercury column even with the "scratch," its length is carefully determined by use of the calibrating engine, provided with a microscope which has a micrometer eye-piece. The column of mercury is shifted exactly its length along the tube, the left hand meniscus resting where the right hand meniscus was before. By repeating the above and weighing the mercury used, the value of the meniscus correction between the limits observed may be calculated.

To move the mercury thread from one position to the other more quickly and to adjust the meniscus with greater ease and precision than had been done before would facilitate a very tedious work. It is believed that the apparatus described below not only serves such a purpose but also provides some security against the loss of the mercury thread when the calibration near the upper end of the manometer is being done. After several days of hard work one may have it all lost in a moment by compressing the air too much in moving the thread near the end of the tube.

A bulb is blown in one end of the manometer tube to be used as a mercury reservoir later. To the other end of the manometer a short piece of tube is sealed which is also provided with a bulb. Rubber tubes are then used to connect as closely as practicable a piece of glass tubing to each end of the manometer tube. These connected tubes are bent at two right angles and return along the front of the calibrating engine till within about ten centimeters apart. Here the tubes are bent at right angles toward the operator. The projecting end of each tube is inserted into one end of a rubber tube which connects them. The rubber tube is longer than the distance between the glass tubes to allow for adjustment of the glass tube to manometer

tubes of varying length; and also to allow the operator full use of the rubber tube without in any way displacing the manometer.

At the middle of the connecting rubber tube a small hole is made. The operator places his thumb and finger on the tube over this hole and by properly compressing the air on one side or the other the column of mercury is forced along the tube in either direction. If too much pressure should force the thread out of the capillary, the bulb at either end would prevent the loss of the mercury and save the work already done.

Another advantage which is obvious, is that the whole space within the connected tubes is protected from dust and moisture during the several days usually required for calibration.

The hole over which the thumb is placed permits immediate equilibrium of pressure as soon as the thumb is removed and prevents any tendency of the mercury to return to any former position by unequal compression of air on the two ends, as might occur if the opening were not provided.

The whole apparatus can be made in a few minutes. It is simple and inexpensive.

A perfectly clean tube is required for the successful manipulation of the mercury thread; otherwise the mercury "crawls" back toward the position from which it is moved for a setting, resulting in serious errors. This "crawling" process is so slow that it may occur unobserved. Thus the worker may exercise the greatest care and still include serious errors, which are not detected until the duplicate settings are made. Even then the same "crawling" of the mercury may produce similar errors which would enable one to get almost the exact duplicate checking data and still be far from the true measurement of the mercury thread lengths in the various positions in the tubes.

The same trouble may arise from any roughening of the capillary by the cleaning fluid used. This should not remain in the tube a great while, in order to avoid such trouble. When clean, the tubes are dried for several hours by passing air through them over calcium chloride by use of the suction pump.

In the calibration above referred to, the shorter the mercury thread used the more accurately is the volume of the capillary determined, provided the weighing of the thread can be very

accurately done. In one case, during the calibration above referred to, an error of three milligrams in the weight of the short thread of mercury resulted in a meniscus correction that was one hundred per cent too large. Evidently, even with the most accurate weighing, it is possible to use a mercury column that is too short. In such case any error made is a large per cent of the quantity weighed. On the other hand, the longer the thread used the greater doubt exists as to the size of the capillary between the thread ends. Threads about 15 millimeters in length were used in this work. Three sets of readings are made for each tube, which check within the limits of experimental error.

Another small aid in this phase of the calibration process consists in a movable light-regulator that is attached to the standard arm of the engine. It, too, is quite simple, but saves time in securing a suitable light on the meniscus of the mercury column. This is often quite difficult during cloudy weather, and at certain positions the proper light for a clear view of the meniscus outline is hard to obtain in good weather. This little attachment consists of a thin board or card-board that is so clamped to the arm of the engine standard that it may be freely rotated by a light touch. This enables the operator to shut off or admit light at any angle which is found best by trial for a clear meniscus. The trouble and time thus saved far outweigh the outlay in making it, because neither the hand nor a card can be so conveniently used. The rotating screen will stand at any angle desired, and can be put on or removed in an instant.

BATHS FOR CONSTANT TEMPERATURE.

Three types of baths have been used in the osmotic pressure work. The first was used for lower temperatures and has been fully described in previous reports.

The second has been briefly described in these pages, and perhaps a more full description of the third kind will embody the essential features of the second so that it may be better understood.

Since the work from 0° C. to 25° C. has been completed the recently constructed baths are for higher temperatures.



A well made box of the size desired is lined with copper, tin-coated. Inside the box is placed a motor-driven stirring apparatus, which lifts the water from the upturned opening of a pipe extending from one end of the bath to the other. By regulating the speed at which the stirring is done, the water in all parts of the bath may be kept at a uniform temperature. For maintaining cooler temperatures a system of pipes conveys a constant stream of cold water through the bath. This is regulated by an overflow standpipe which exerts constant pressure upon the water passing through the bath.

A loop of the pipe through which the stirring apparatus draws the water is extended outside the end of the bath. This loop is heated by gas burners up nearly to the desired temperature. The few degrees more required are supplied by electric stoves, placed in cylinders of copper that extend into the bath, or entirely from one side to the other, and are closed with brass caps. To prevent sparking at the contact point of the mercury and platinum wire in the thermo-regulator and also on the relays which are used to control the current, condensers are used. These are made of tinfoil placed between paraffined paper. In order to operate the bath at different temperatures more or less gas is used. The small difference of heat above referred to is gotten from the electric current.

In order to prevent evaporation of the bath water and the formation of mist on the glass door through which the readings of the manometer are taken, it is necessary to separate the upper portion of the bath from the lower. For this purpose a brass plate covers the lower part containing water. Heavy weighted cans, open at the top, extend through the brass plate into the water. The cans are large enough and deep enough to enclose the bottle containing the cell and all the portions of the manometer where the mercury reservoirs are. The can is then carefully covered by a thick heat-insulating pad, so that only very slight change of temperature takes place when it becomes necessary to open the bath.

The upper section of the bath is so constructed that it may be removed, being clamped to the lower part by sash locks. Rubber strips lie between the two sections and insure close con-

tact. A thermo-regulator controls electric lamps in the upper portion, as below, and uniform temperature in the air space is secured by use of an electric fan. For higher temperatures the air space is heated nearly to the desired temperature by a system of water pipes through which hot water is circulated by a stirring apparatus similar to the one described for the main bath. The pipes are situated at one end of the bath just behind the electric fan, but are connected with the stirring apparatus and the gas flames on the outside of the bath. The whole bath is placed upon a support as free from vibration as possible. Beams pass through openings in the floor to the wall below and upon these the bath is put. Three or four such supports are now in use.

Another feature which avoids vibration is the method of gearing the motor to the water pump or stirrer. On the motor shaft is placed a contact pulley. A belt transmits power to the water pump. All of this has a separate support from the bath, but very little vibration is produced.

The cathetometer used in observations together with the brass meter scale is also supported on the beams above referred to. All manometer observations are referred to the "scratch" or mark etched on the glass, and the distance between the upper and lower limits of the nitrogen in the manometer is determined by the use of the meter scale viewed through the telescope of the cathetometer. In these observations it is necessary to bring the telescope to a focus always from the same direction because of the "back lash" of the adjustment screw.

Thus arranged the bath keeps constant temperature for months.

THE NICKEL FERROCYANIDE CELLS.

A more abundant supply of suitable cells recently made practicable further investigation of other new, electrolytically precipitated membranes. For purposes of record and identification the cells used in this investigation are marked Ni₁, Ni₂, Ni₃, and so on. Their behavior during the removal of air from the cell walls and upon the deposition of membrane will be noted first. The cells used during this work were Ni₁, Ni₂, Ni₃, Ni₄, Ni₅, Ni₆. They will be taken up in the order given.

Number one and number two were started together at the beginning of the work.

The pores of Ni_1 were somewhat less open than those of Ni_2 , as shown by the current that passed in each case when the air was being removed and also when the membrane was deposited. Further comparison of these two cells is impossible because Ni_1 was burst by the manometer cone in being set up before any osmotic record for this cell was established.

This was doubtless due to a baking crack which was not visible.

Ni_2 , however, has the best record of any one of the series. It was prepared as indicated in the preliminary statements. From the amount of current which still passes through it when membrane is deposited, it seems to be the least dense of the six cells. It was first set up for a trial measurement on Nov. 23, 1910, with a normal cane sugar solution at 25° . Within an hour it had developed an osmotic pressure of approximately twenty-five atmospheres. From eight minutes past twelve to one o'clock the mercury rose steadily in a closed manometer without any oscillation through two hundred and twenty-six millimeters.

For six days the pressure remained fairly constant but a loss of $1^\circ.7$ occurred in the rotation of the solution from the cell. This was probably due to the dilution caused by the development of the entire pressure by osmosis; resulting in the entrance of a relatively large amount of water and dilution. As a quantitative test this was not of much value, but the behavior was considered promising.

Several subsequent attempts to secure a measurement failed on account of a leak at the washer of the needle tube or other assignable cause all of which were in no way dependent on the membrane. For the measurements later developed with this cell, see experiments 1, 2, and 5, on the following pages.

Ni_3 met the same fate that befell Ni_1 and hence it has no record.

Ni_4 of all the cells showed the most irregular passage of the electric current in the removal of air from the cell and in the membrane deposition. A few times the resistance has reached

about one-half million ohms, but only after several months, with repeated deposition of membrane; and this resistance varies. So far no successful use has been made of Ni_4 , though recently it gave some promise of more normal activity.

Ni_8 and Ni_5 are the only nickel ferrocyanide cells besides Ni_2 that we have so far used successfully to measure osmotic pressure. This does not mean, however, that any one of those that are still intact is unfit for such measurement. In this connection it should be kept in mind that if any one of a large number of conditions is abnormal, no true measure of osmosis is possible. This accounts for the relatively large number of experiments which must be performed in order to produce and maintain proper conditions that fail in no point.

Ni_5 showed a dense texture throughout. After membrane had been deposited on Feb. 2 for an hour and ten minutes, on Feb. 3 for an hour and ten minutes, and on Feb. 6 for an hour and thirty minutes, the cell showed a resistance recorded during these three periods of twelve thousand ohms. Comparing Ni_5 with Ni_2 for similar conditions, we find the highest resistance in Ni_2 to be fifty-seven thousand ohms. The least resistance offered by Ni_2 in this time was ten thousand ohms.

Ni_5 was used in experiment three herein recorded. So far as known no membrane has ever been developed in a shorter time than was required for this one to produce a measurement. This point is more fully presented in the general discussion of the nickel ferrocyanide membrane later on.

Ni_8 in its density and resistance to the electric current is very similar to Ni_5 , perhaps as nearly alike as two cells could be found. In both of these, the membrane, as shown by a steadily decreasing current, has been deposited with regularity and uniformity. Each one offers about a half million ohms resistance at the end of a brief deposition of fresh membrane.

Below are presented several results with the use of the cells just described:

EXPERIMENT I.

Concentration, 0.1 weight normal cane sugar solution; rotation of original solution, $12^\circ.7$; rotation at the end of the experiment, $12^\circ.7$; loss in rotation, 0; volume of nitrogen in the

manometer, 454.14; time set up, 2 P. M., Jan. 6, 1911; manometer, 9; cell used Ni_2 ; resistance of membrane, 64,705 ohms; initial pressure a little below the theoretical for these conditions; pressure of mercury, 409; pressure of the solution, .01; capillary depression, .02. Below is table I. with corrections applied.

Table I.

Time	Temp.	Atmos. Pres.	Corrected	Pressure		Ratio
			Vol. of N_2	Osmotic	Gas	
Jan. 7	25°C.	.999	155.69	2.624	2.431	1.080
" 8	"	.993	155.51	2.635	"	1.084
Average						1.082
The ratio formerly established by the $\text{Cu}_2\text{Fe}(\text{Cn})_6$ cells						
for these conditions is						1.084

EXPERIMENT II.

Concentration, 0.1 weight normal; rotation of solution before and after the experiment, 12.70; manometer 9; cell used, Ni_2 ; set up 1 P. M., Jan. 13, 1911; volume of N_2 in manometer, 454.14 calibration units; resistance of membrane, 70,000 ohms; corrections: liquids in manometer, 0.418; capillary depression, 0.02.

Table II.

Time	Temp.	Atmos. Pres.	Corrected	Pressure		Ratio
			Vol. of N_2	Osmotic	Gas	
Jan. 15	15°C.	0.991	147.08	2.533	2.349	1.078
" 16	"	1.010	146.72	2.523	"	1.074
" 17	"	1.011	146.68	2.523	"	1.074
" 18	"	1.014	146.61	2.517	"	1.072
Average		1.006		Average		1.074

Average total pressure, 3.531; corrected, 2.525.

When corrected by normal atmospheric pressure, the ratio is 1.078

The average ratio established with the copper ferrocyanide for the same conditions is 1.082

EXPERIMENT III.

Concentration, 0.1 weight normal; rotation of solution before and after the experiment, 12.70; manometer, 1; cell used, Ni₅; set up at noon Feb. 18, 1911; volume of N₂ in manometer is 445.43; membrane resistance, 104,000 ohms; corrections: liquids in manometer, .438; capillary depression, 0.02.

Table III.

Time	Temp.	Atmos. Pres.	{	Corrected	Pressure		Ratio
					Vol. of N ₂	Osmotic	
Feb. 19	15°C.	1.001		144.31	2.544	2.349	1.083
" 20	"	0.989		144.73	2.547	"	1.084
" 21	"	1.006		144.47	2.536	"	1.081
" 22	"	1.001		144.62	2.537	"	1.080
Average		0.999			Average		1.082
Average total pressure is 3.540; corrected,					2.541.		
Average ratio for copper ferrocyanide is					.	.	1.082

EXPERIMENT IV.

Concentration, 0.6; rotation before and after the experiment, 69°.2; manometer, ①; cell used, Ni₆; set up Mar. 29, 1911, 4 P. M.; volume of N₂ in manometer, 445.43; resistance of membrane, 570,000 ohms; corrections: liquids in manometer, 0.642; capillary depression, 0.02.

Table IV.

Time	Temp.	Atmos. Pres.	Corrected	Pressure		Ratio
			Vol. of N ₂	Osmotic	Gas	
Mar. 30	30°	0.975	27.642	15.802	14.830	1.066
" 31	"	0.988	27.578	15.826	"	1.067
Apr. 1	"	0.997	27.508	15.859	"	1.069
" 2	"	1.005	27.556	15.822	"	1.067
" 3	"	1.009	27.561	15.814	"	1.066
" 4	"	1.009	27.574	15.807	"	1.066

Average ratio is 1.067

Average for copper ferrocyanide of this concentration at 30° yet to be determined.

EXPERIMENT V.

Concentration, 0.1 weight normal; rotation of the solution before and after the experiment, 12.75; manometer, 1; cell used, Ni₂; set up 4 P. M., Apr. 6, 1911; volume of N₂ in manometer, 445.43; resistance of membrane, 142,500 ohms; corrections: liquids in manometer, .435; capillary depression, 0.02.

Table V.

Time	Temp.	Atmos. Pres.	Corrected Vol. of N ₂	Pressure		Ratio
				Osmotic	Gas	
Apr. 22	30°	0.995	146.99	2.480	2.472	1.004
" 23	"	1.006	146.19	2.486	"	1.006
" 24	"	1.006	146.44	2.482	"	1.004
" 25	"	1.006	146.88	2.471	"	1.000
" 26	"	1.009	146.72	2.472	"	1.000
" 28	"	1.010	146.52	2.474	"	1.001
" 29	"	1.000	147.37	2.467	"	0.998
" 30	"	0.990	147.48	2.473	"	0.999
Average		1.003		Average		1.001

Average total pressure is 3.478.

Average total pressure corrected by the average atmospheric pressure is 2.475.

GENERAL DISCUSSION.

One of many requirements for a proper membrane to measure osmotic pressure is that it shall not affect the solution used. To determine whether the nickel ferrocyanide causes any inversion of cane sugar, two tests were made.

The first was by the use of Fehling Solution, which showed no indication of inversion.

The second consisted in the addition of some precipitated nickel ferrocyanide, which was entirely free from other electrolytes, to a sugar solution of known concentration and rotation.

A saccharimeter tube was used in order to take observations from time to time of the rotation. On Jan. 16 the colloid and a sugar solution, whose rotation and concentration had just been determined, were mixed. The rotation was retaken at once to

see the initial state produced. On Jan. 17 there was no change in rotation. On Jan. 27 no change had occurred, none on Jan. 30, and on Feb. 13 the rotation was still the same. The whole time was 28 days. The temperature was about 20°C. The sugar solution was taken from some that had been prepared to use in a measurement. Hence the potassium ferrocyanide and the thousandth normal thymol solution were both present just as in taking a measurement. So far as can be seen, there is no inversion of the solution in the cell, caused by the action of the membrane.

ACTIVITY.

When the copper ferrocyanide membrane is used for some time—two or three years,—its activity in some cases falls off to such an extent that much time is required for the development of maximum pressure. Because there are so many possibilities of failure in measuring osmosis, the chances for success are greatly increased by shortening the time required for reaching maximum pressure. It is quite possible that nickel ferrocyanide as a membrane will also come to similar sluggish action with equal age. So far, however, this tendency has not appeared in the oldest cell, which has been in use seven months. By reference to the record of Ni_2 , some idea of the activity of the membrane in the beginning is obtained. At the present time if a cell is placed in the bath for a measurement only a few hours elapse before a maximum pressure is exerted.

As already indicated, a large per cent of the efforts to measure osmotic pressure fail because it is so difficult to have all necessary conditions fulfilled. One of the chief difficulties, prior to the work done in this laboratory, was the lack of a good membrane in a suitable cell and at the proper place in the cell. In nearly all cases of failure to obtain satisfactory results in this work with the nickel ferrocyanide membrane, the trouble has been traced to other causes than defects in the membrane or in the cell.

No special duration tests have been made, but one experiment extended over twenty-four days with unimpaired membrane at the conclusion of the experiment.

MEASURING LOW CONCENTRATIONS.

There is not much evidence to show that this membrane responds promptly to barometric changes, although this property may be expected to accompany a membrane which shows such activity. In measuring the pressure of dilute solutions much difficulty is found in obtaining concordant ratios, due largely to the lag in the response of the cell to changes of atmospheric pressure. The corrections made for barometric readings are not true expressions of the air pressure then in effect through the membrane, especially at times of sudden changes in the weight of the atmosphere. Any error thus made is so large a per cent of the quantity measured that the relative effect on the ratio of osmotic to gas pressure is large. In order to equalize these effects the average of all barometric readings is used to correct the average of all the total pressures exerted. The effect of this is seen in experiment 5.

This response is doubtless more prompt at higher temperatures. Consequently less trouble would be expected from this cause at forty degrees than at ten or fifteen degrees. Experience bears this out.

The nickel ferrocyanide membrane was used some during the present year to measure the pressure of one-tenth normal solutions due to the greater lag of the older copper ferrocyanide membranes in responding to atmospheric changes. And it may be that with older nickel ferrocyanide cells the same trouble would exist. This remains for time to test. Since there were also new copper ferrocyanide cells in use in this work, the weight of evidence is somewhat in favor of the view that the activity of the nickel ferrocyanide membrane produces a more prompt response to changes in atmospheric pressure. This may not prove to be true of all such cells, because it is to be noted that most of this work on one-tenth normal solutions was done with the most active of all the nickel ferrocyanide cells. But here attention is called to experiment three, in which Ni_5 was used. This cell, as already stated, is dense and any changes of atmospheric pressure would be slower in producing an effect with Ni_5 than with the more porous Ni_2 , if cells of different densities exert any influence in the matter. But by comparing the ratios obtained

in the two experiments, No. 2 and No. 3, those of the more dense and supposedly less active cell are the more nearly constant, although other conditions were nearly the same.

Manometer 9 and manometer ① have been compared and found to agree. The variations of the barometer extended over eleven-thousandth of an atmosphere in each case. The duration was the same in both cases, both were at 15°C. and tenth normal concentration. Again the evidence seems to point to some property of the membrane for prompt action, but more evidence is necessary before any conclusion can be reached.

In general the resistance of the copper ferrocyanide membrane to the current is greater than that of the nickel compound. Whether longer use and age will produce a change in this respect is a matter for future observation. Also, whether this is an advantage or a disadvantage is not known.

By reference again to the tables it is seen that experiment No. 3 shows an average ratio of osmotic to gas pressure of 1.082, with .01 normal concentration at 15°C. But No. 5 of the same concentration with a temperature of 30° gives a ratio of unity.

The average ratio of all concentrations between 0°C. and 25°C. is 1.083. Up to 25° stability seems to exist. At 30° and at 40° the ratio is unity. If the same is found at higher temperatures the Law of Boyle as well as that of Gay Lussac will be demonstrated to apply to osmotic pressure, as to gas pressure. It has already been demonstrated by the work between 0° and 25° that the Law of Gay Lussac holds between those limits for all concentrations up to the weight normal. The final pressure of a 0.1 normal solution at 30° is the same as that which the solution would be if its volume were confined to the volume of the solvent.

What causes the change in osmotic pressure of dilute solutions between 25° and 30° is not known. It seems possible that hydration changes may produce dilution. Whatever the cause, the process is one which requires some time. At first a pressure is developed which nearly equals that at 25° and then it gradually decreases to constant theoretical gas pressure. In several cases this has been the relative behavior, and about a month is required for a measurement of this kind. Experiment

5 was begun Apr. 6 and did not develop constant pressure or equilibrium until Apr. 21. From Apr. 21 till May 1, there was constant pressure as shown in the table (5).

The element of time required for the deposition of membranes of sufficient strength to withstand maximum pressures is of some interest. Repeated subjection of the cell to the current through the two solutions, as already described, is necessary in order to secure sufficient stability or thickness of membrane to withstand the higher osmotic pressure exerted upon it. Alternate soaking and depositing produce the desired results. The exact effect of soaking the cells is not definitely known, but it seems probable that practically all ionic or non-colloidal material is thus removed, resulting in a more homogeneous membrane; and also less subject to attack by any solutions coming against it. Summing up all the time required for the quickest deposition of a copper ferrocyanide membrane and the shortest time required for a nickel ferrocyanide membrane, each giving a measurement, we have the following for comparison: the copper ferrocyanide required 28 hours; the time required by the nickel ferrocyanide was ten hours and forty-six minutes. Whether any advantage besides the saving of time is to be derived from this fact cannot be stated.

It will be recalled that in depositing membrane the potassium ferrocyanide within the cell is frequently renewed, by pouring fresh solution through the funnel set in the cell. The funnel extends nearly to the bottom of the cell, and the end of the exit tube is just below the rubber stopper, so that the fresh solution enters at the bottom, forcing the solution already in the cell upward and out the exit tube. In this way there is an upward flow around the electrode. If the amperage is noted while the replacement of the solution is taking place it is found that quite an increase of current flows. In one case where the resistance before pouring in fresh potassium ferrocyanide was 110,000 ohms, it became only 55,000 while the solution was being changed. The current in this instance was doubled.

The explanation suggested for this is similar to that given for the rotating anode in electrolytic work. But if the solution in the cell is agitated by moving the funnel supporting the

electrode, no such change is seen in the current flow. In fact, no difference in the current is observed with this treatment.

When the liquid has ceased to flow from the cell, after a pouring, the current invariably decreases till it becomes the same that it was before the change of solution, so that the cause can not be in the difference of the two solutions. It is possible that the force of the flowing liquid produces a mechanical disturbance which reduces the resistance for the time.

Whether any importance is to be attached to this phenomenon is not known. The facts are recorded, but the explanations suggested may not be correct.

OSMOTIC PRESSURE IS NOT A FUNCTION OF THE MEMBRANE USED.

Until the present year only the copper ferrocyanide membrane was used in the quantitative determination of osmotic pressure, and while it has been supposed that the nature of the membrane was not a factor in osmosis, no comparison of quantitative results obtained by different kinds of membrane has before been possible. Some comparisons of the measurements obtained with both membranes appear in the tables. It will be seen that they agree quite as well as duplicate measurements with the same membrane. Here we have ample experimental evidence for the conclusion that osmotic pressure is not a function of the membrane used.



